LA-UR-15-22407
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Title: Characterization and testing of crystalline ceramic waste forms

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Intended for: DOE-Office of Nuclear Energy-milestone report

Issued: 2015-04-03

Characterization and testing of crystalline ceramic waste forms

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Material Recovery & Waste Form Development Campaign
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September 30, 2014
FCRD-SWF-2014-000250

Name/Title of Deliverable/Milestone	Characterization and testing of crystalline ceramic waste forms **M3FT-14LA0308011**
Work Package Title and Number	Advanced Waste Form (Ceramic)-LANL **FT-14LA030801**
Work Package WBS Number	**1.02.03.08**
Responsible Work Package Manager	Ming Tang *(Name/Signature)*
Date Submitted	*09/30/2014*

Quality Rigor Level for Deliverable/Milestone

☒ *Rigor Level 3* ☐ *Rigor Level 2* ☐ *Rigor Level 1* ☐ *Nuclear Data*

This deliverable was prepared in accordance with Ming Tang *(Participant's Name)*

QA program which meets the requirements of

☐ *DOE Order 414.1* ☐ *NQA-1-2000*

This Deliverable was subjected to:

☒ *Independent Technical Review* ☐ *Peer Review*

Independent Technical Review (ITR)	***Peer Review (PR)***
Review Documentation Provided	***Review Documentation Provided***
☐ *Signed ITR Report or,*	☐ *Signed PR Report or,*
☐ *Signed ITR Concurrence Sheet or,*	☐ *Signed PR Concurrence Sheet or,*
☒ *Signature of ITR Reviewer(s) below*	☐ *Signature of PR Reviewer(s) below*

Name and Signature of Peer Reviewers(s)/Independent Technical Reviewer(s)

Cheng Sun

SUMMARY

The research conducted in this work package is to collect data in support of future development of ceramic waste forms and to help develop the next generation high performance waste management technologies. This work package collaborates closely with the work conducted under “Advanced Waste Forms (Ceramics) - Savannah River National Laboratory (SRNL) - (FT-14SR030802)” and the NEUP project “Alternative High-Performance Ceramic Waste Forms” – Alfred University (AU) – (DE-AC07-05ID14517)”.

The Los Alamos National Laboratory (LANL) is focusing on characterization and radiation stability testing procedure on the reference crystalline ceramics to further develop the crystalline ceramic waste form to incorporate combined HLW raffinate stream and/or TRU stream from fuels fabrication processes. In Fiscal Year 2014, we are mainly working on various hollandite phase (e.g. $BaAl_2Ti_6O_{16}$) materials including different compositions, different fabrication routes, and single phase vs. multiphase. Various characterization techniques (including X-ray diffraction, transmission electron microscopy, scanning electron microscopy) were used to characterize these samples. For the radiation stability test, selected hollandite samples were exposed to either heavy ion (Kr) or light ion (He) radiations environments at room temperature to test their radiation stability. We also investigate radiation stability on single phase powellite and powellite phase in multiphase waste forms.

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1. Hollandite

Hollandite phase has been found as major crystalline phase in several of the different ceramic waste form formulations that have been proposed [1-3]. Hollandite compounds are represented by the general formula $A_xB_8O_{16}$ ($x < 2$). This formula is somewhat deceptive since the A cation may be monovalent (Na, K, Rb, Cs, Tl) or divalent (Sr, Ba and Pb) or a combination of both. Depending on the choice of the A-type cations a range of cations with valences in the range +2, to +5 may occupy the B site. Cations found in the smaller B-site of hollandites include Zn, Cr, Mn, Fe, Co, Al, Ga, Rh, Zr, Ti and Mo. The hollandite structure consists of a framework of TiO_6 octahedra which share edges and corners to form square channels or tunnels. These tunnels, which contain box-shaped cavities of eight oxygen ions (A sites), can accommodate a wide variety of large cations such as Cs^+ and Ba^{2+}. This characteristic is particularly useful for ^{137}Cs immobilization, as ^{137}Cs transforms to ^{137}Ba through beta decay with a half-life of about 30 yr and the accommodativeness of both Cs and Ba in the hollandite structure ensures its stability over the decay period and beyond. Radiation damage effects have been studied by using natural minerals that contain actinides, actinide-doping, and ion irradiations [4-7].

In this study, single phase Cr-hollandite and CAF-hollandite samples fabricated using melt-pressing and spark plasma sintering (SPS) techniques at the Alfred University (AU) and multiphase Cr-hollandite and CAF-hollandite samples fabricated using SPS and high press (HP) techniques at The Savannah River National Laboratory (SRNL), are characterized with transmission electron microscopy (TEM) and grazing incidence X-ray diffraction (GIXRD) at LANL. Radiation stability of these compounds is tested under ion irradiations.

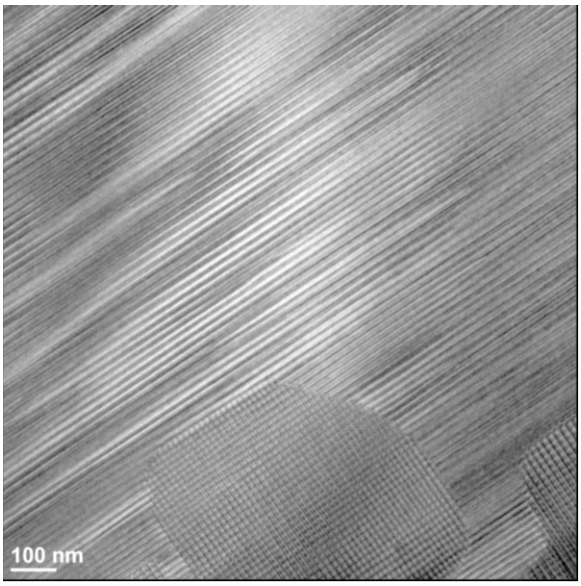
1.1 Single phase hollandites

Single phase Cr- and CAF-hollandite samples were fabricated at AU by melt-pressing and SPS. TEM results reveal a unique polysomatic structure feature in pristine hollandite sample. And experiment results show that single phase hollandites are susceptible radiation-induced amrophiztion, which is similar to the hollanidite phase in multiphase waste forms.

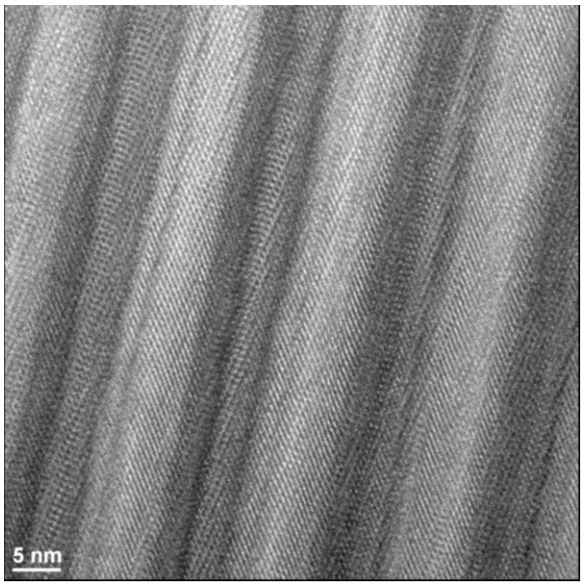
1.1.1 TEM observation on pristine single phase Cr-hollandite

Figure 1 is the TEM observation on a pristine single phase Cr-hollandite sample fabricated by melt-pressing. The TEM sample was prepared using focus ion beam (FIB) technique. The images show various planar features in this sample. These types of planar features can be

described as intergrowth structures, using the formalism of polysomatism [8], in which the crystal is regarded as made of chemically distinct layer modules. A polysomatic series is a group of crystalline compounds that possess the same types of modules in different rations or sequences.



(a)



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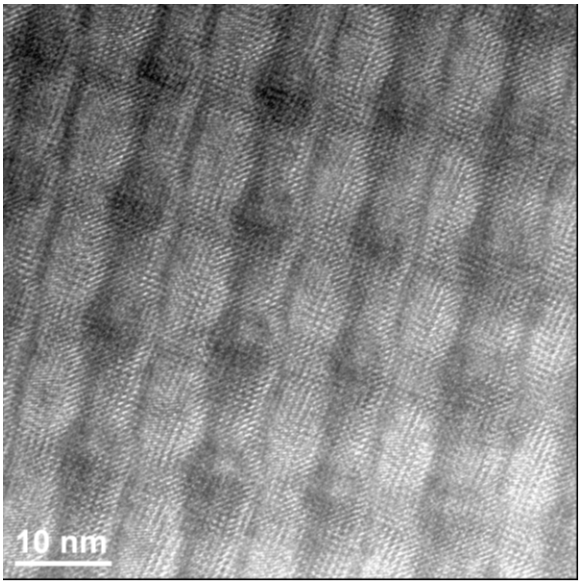


(c)

Figure 1. TEM micrographs of pristine single phase Cr-hollandite. (a) Bright field image, (b) and (c) high resolution TEM images.

The polysomatic reaction could be referred to as solid-state reactions, which involve solids as both reactant and product. In solid-state reactions, the orientation of the product can be strongly controlled by the reactant crystal structure. Such reactions are sometimes called topotactic or

topotaxic to denote the three-dimensional orientation relationship. In cases where both the reactant and products are members of the same polysomatic series, such reactions commonly occur by a mechanism that involves nucleation and growth of narrow slabs of the product mineral. Thus, a slab of the reactant structure is replaced by a slab having a different sequence of modules.

1.1.2 Radiation stability test on single phase hollandites

Single phase Cr- and CAF hollandite samples were subjected to 600 keV Kr and 200 keV He ion irradiations at room temperature to test their radiation stability. Heavy ions (e.g. Kr) are used to simulate energetic recoil nuclei interaction which involves ballistic processes, especially for alpha decay; while light ions (e.g. He) are used to study the role of ionization on the structural evolution in crystalline structures. Figure 2 shows the GIXRD results of melt-pressed Cr-hollandite and CAF-hollandite samples before and after 600 keV Kr ion irradiations up to the fluence of 2.5×10^{15} ions/cm^2 (corresponding to a dose of 5 dpa). The small diffuse scatterings observed between 26-32° 2 theta range (see arrows in Fig. 2), suggest the onset of irradiation-induced amorphization in both single phase Cr- and CAF-hollandites. Cross-sectional TEM observations in Figure 3 confirm that Cr-hollandite phase undergoes an irradiation-induced amrophization at a fluence of 2.5×10^{15} Kr/cm^2 (~ 5 dpa). Figure 3 (c) shows the high resolution TEM image of interface between amorphous and hollandite phase in the irradiated layer.

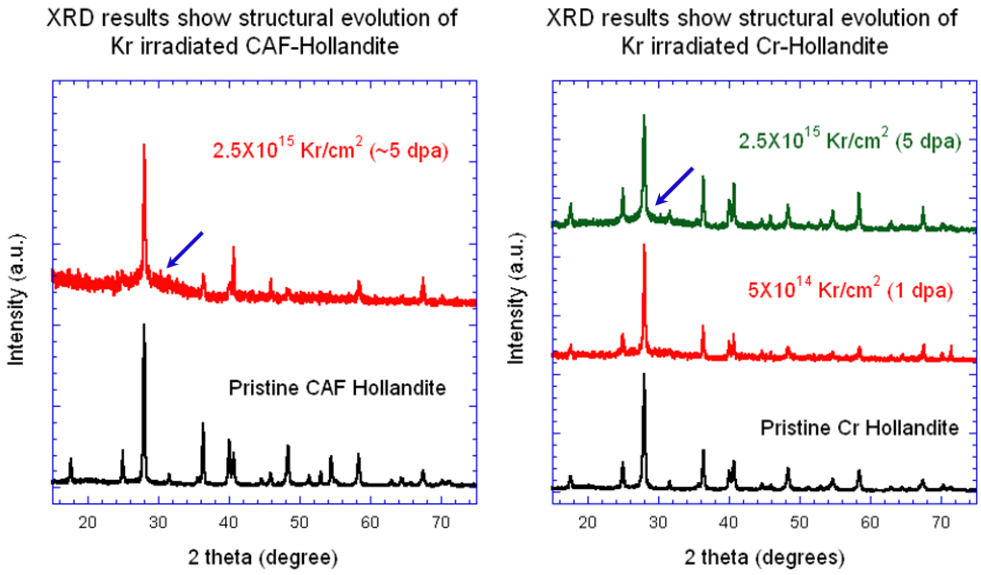
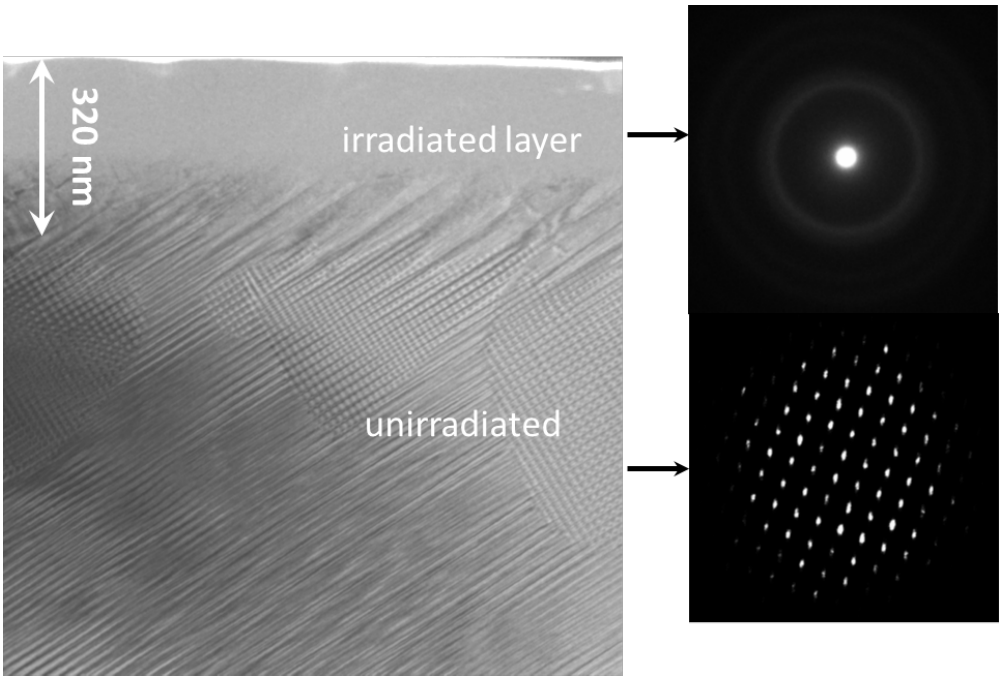
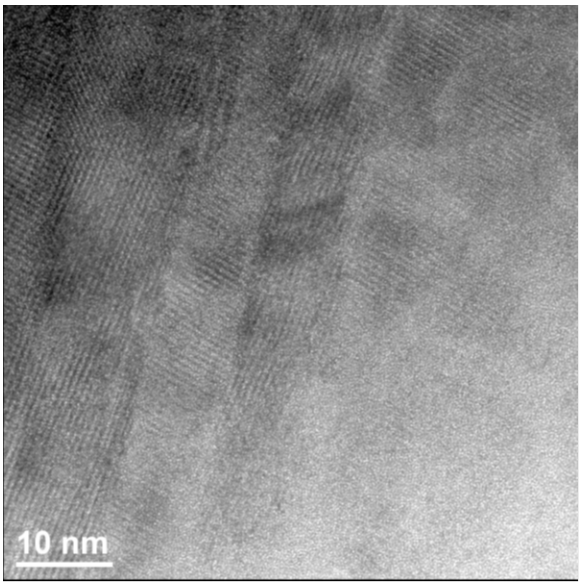


Figure 2. XRD results of single phase CAF-hollandite (left) and Cr-hollandite (right) before & after 600 keV Kr irradiation.



(a)



(b)

Figure 3. (a) Cross-sectional TEM micrograph of single phase Cr-hollandite irradiated with 600 keV Kr ions to a fluence of 2.5 ×10^{15} Kr/cm^2 (~5 dpa) and selected area electron diffraction (SAED) patterns corresponding to irradiated layer and unirradiated area, respectively; (b) High resolution image of interface between amorphous and hollandite phase.

TEM results in Figure 4 show that hollandite phase in multiphase ceramic waste form material CW-AFHZCa100 is susceptible to radiation-induced amorphization under 600 keV Kr ion irradiation at a fluence of 2.5 × 10^{15} ions/cm^2 (corresponding to a dose of 5 dpa). The chemical composition was determined by EDS at STEM mode, and the crystal structure was identified by

indexing the electron diffraction pattern. Experimental results reveal that hollandite phase in multiphase waste form shows the similar radiation response to the corresponding single phase under the similar radiation condition.

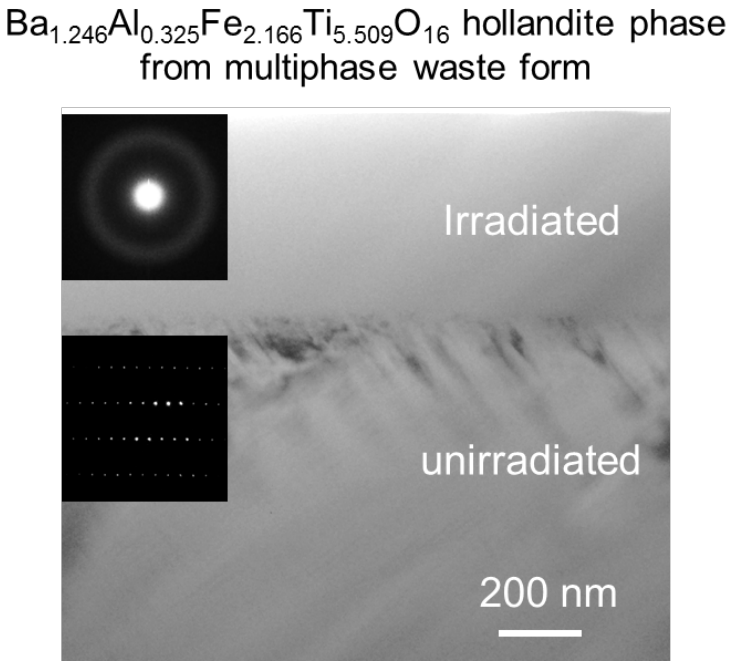


Figure 4. Cross-sectional TEM micrograph of hollandite in CW-AFHZCa100 multiphase ceramic waste form irradiated with 600 keV Kr ions to a fluence of 2.5 $\times 10^{15}$ Kr/cm^2 (~5 dpa) and inset SAED patterns corresponding to irradiated layer and unirradiated area, respectively.

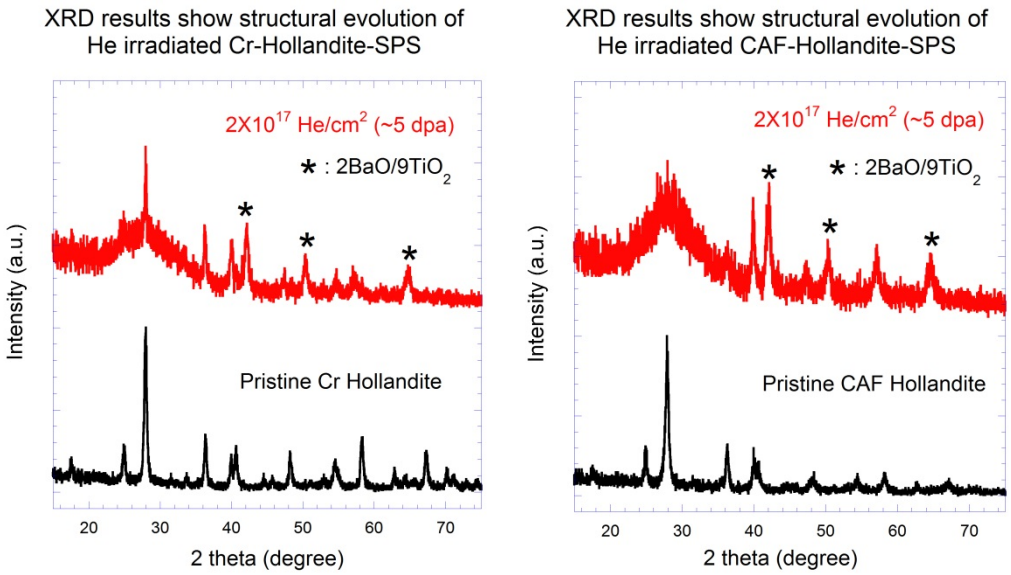


Figure 5. XRD results of single phase CAF-hollandite (right) and Cr-hollandite (left) before & after 200 keV He irradiation.

In this task, SPS synthesized single phase hollandites were exposed to 200 keV He ions at room temperature. GIXRD results in Figure 5 shows an irradiation-induced amorphization observed in both single phase Cr- and CAF-hollandites under 200 keV He irradiations. Also, some new diffraction peaks other than hollandite phase appear after ion irradiation, and these peaks could be indexed as $2BaO/9TiO_2$ phase. It suggests that a phase decomposition occurred in He irradiated hollandites.

1.2 Multiphase hollandite

Multiphase Cr-hollandite and CAF-hollandite samples were fabricated at the SRNL by HP and SPS. Besides the major phase hollandite, these multiphase samples possess perovskite, zirconolite and other minor phases. Radiation stability test reveals that these multiphase hollandites undergo amorphization and decomposition under ion irradiations.

1.2.1 XRD results on pristine multiphase hollandites

XRD data of different multiphase hollandites are shown in Figure 6. All of peaks in XRD plots of four multiphase samples are indexed to three predominant phases, hollandites, perovskites, and zirconolites along with traces of unknown minor phases. There is no big difference between HP and SPS synthesized.

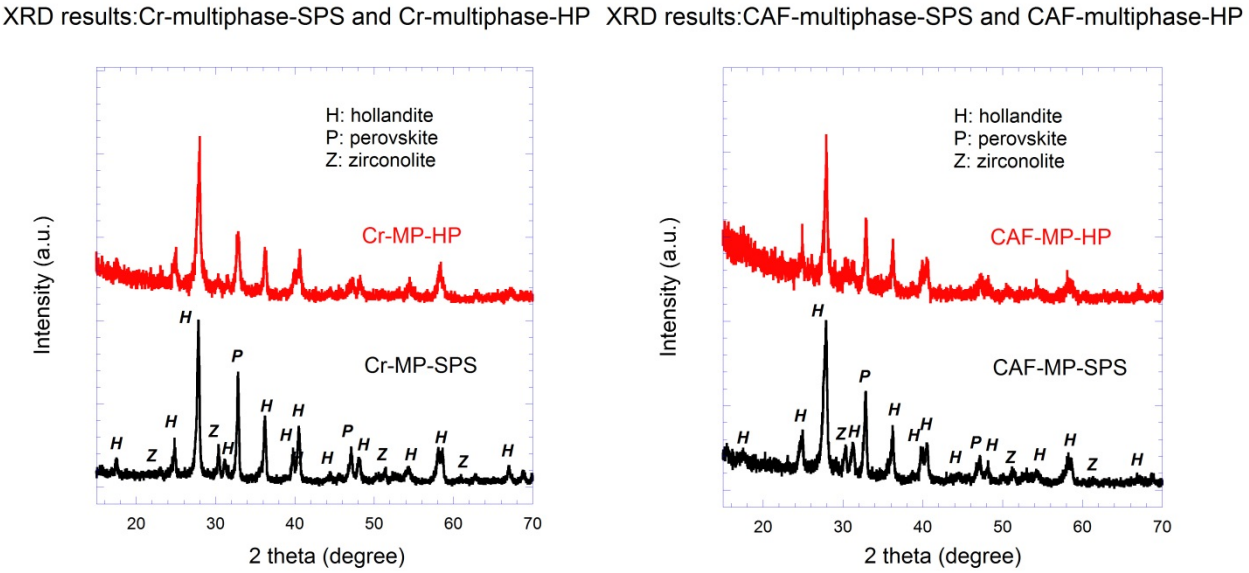


Figure 6. XRD results of multiphase phase CAF-hollandite (right) and Cr-hollandite (left) fabricated using HP and SPS.

1.2.2 Radiation stability tests on multiphase hollandites

These multiphase hollandite samples undergo ion irradiations with 200 keV He ions at room temperature. Figure 7 and 8 show GIXRD observations of structural evolution in these samples before and after He irradiation to a dose of 5 dpa. Similar radiation response as single phase hollandites, is observed in these multiphase hollandites. Radiation-induced amorphization and phase decomposition occur in both multiphase Cr- and CAF-hollandites fabricated in different routes.

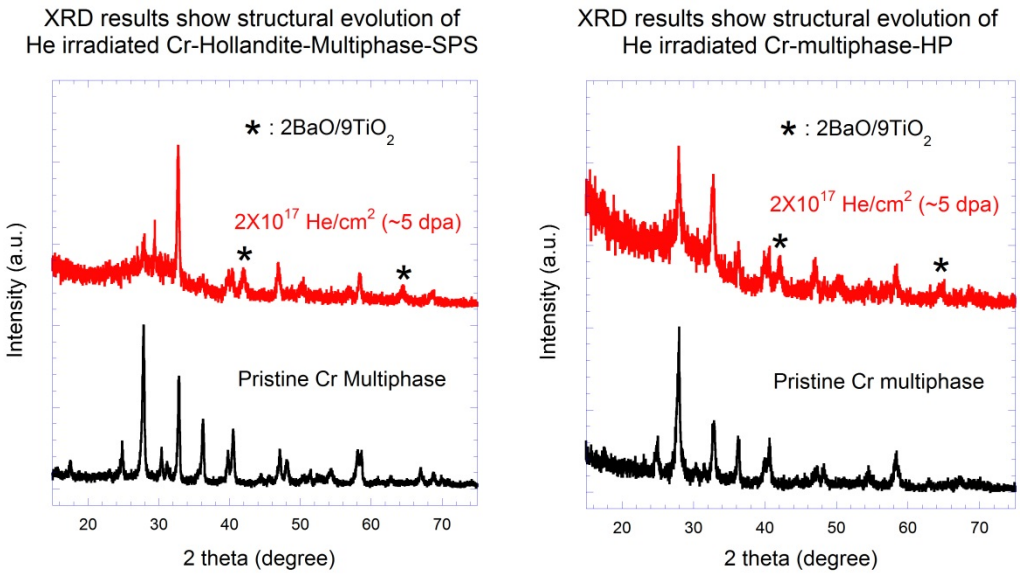


Figure 7. XRD results of multiphase Cr-hollandite fabricated using HP (right) & SPS (left) before & after 200 keV He irradiation.

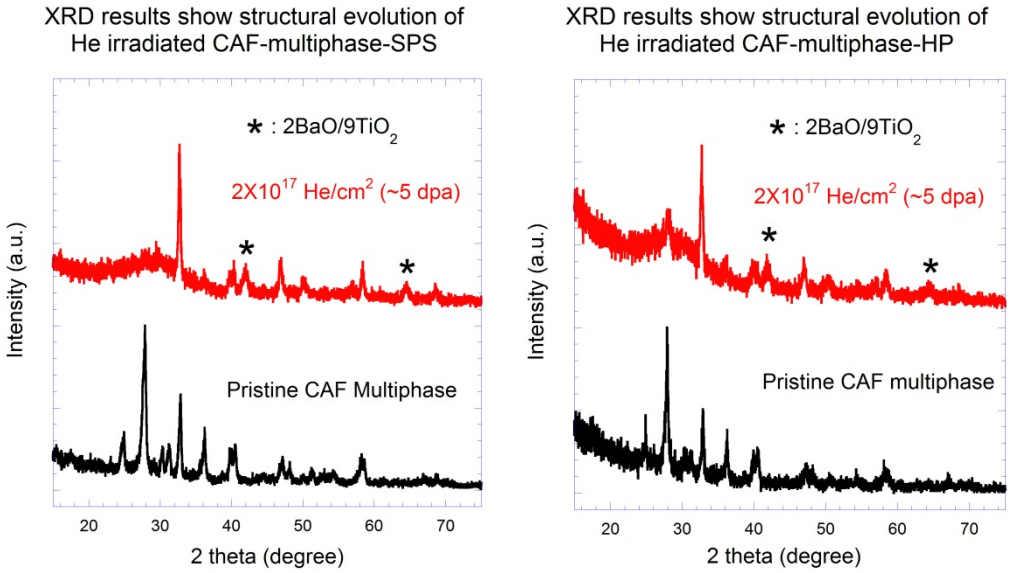


Figure 8. XRD results of multiphase CAF-hollandite fabricated using HP (right) & SPS (left) before & after 200 keV He irradiation.

2. Powellite

Powellite is a molybdate mineral with a chemical formula of $CaMoO_4$ or $BaMoO_4$, and a tetragonal structure. Due to its structural variability, powellite can accommodate considerable chemical substitutions including trivalent actinides and lanthanide elements. As a primary Mo containing crystalline phase, powellite phase has been observed and studied as a component of multiphase waste form systems [9, 10]. The radiation effects in multiphase glass ceramic and crystalline ceramic waste forms have been initiated, however little is known regarding the behavior of crystalline molybdate materials such as powellite.

In order to investigate the radiation stability of powellite phase, single phase $BaMoO_4$ and $CaMoO_4$ in multiphase glass ceramic waste form (Mo-6.25) were irradiated at the same ion irradiation conditions to explore radiation tolerance of powellite phase in multiphase waste forms and compare to the single phase powellite. 600 keV Kr and 200 keV He irradiations at room temperature were used to simulate alpha decay and alpha particle radiation in nuclear wastes.

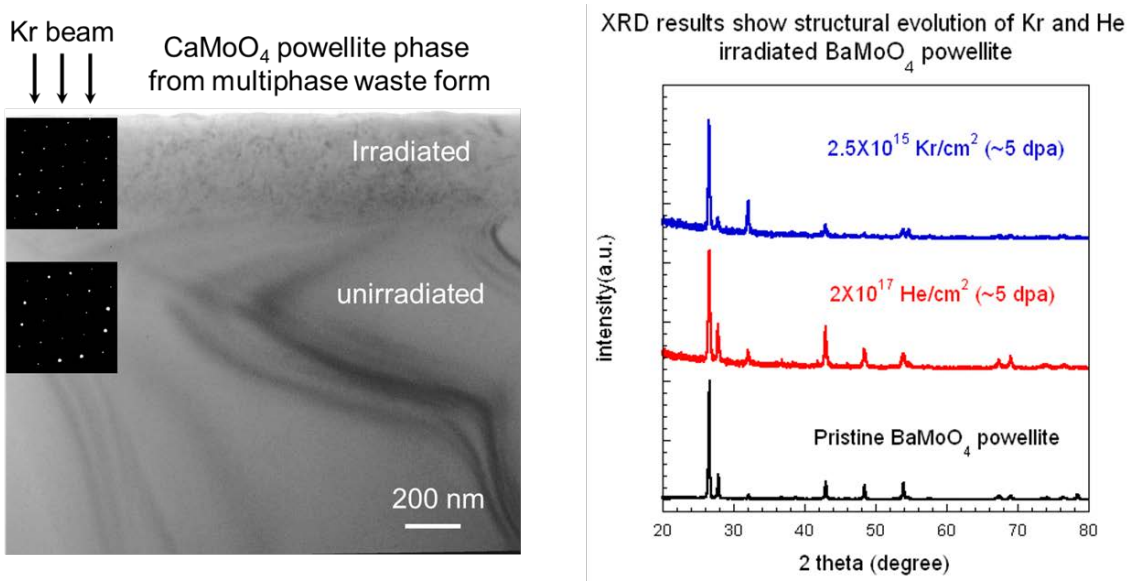


Figure 9. Cross-sectional TEM micrograph (left) of powellite in Mo-6.25 multiphase glass ceramic waste form irradiated with 600 keV Kr ions to a fluence of 2.5×10^{15} Kr/cm^2 (~5 dpa) and inset SAED patterns corresponding to irradiated layer and unirradiated area, respectively; XRD results (right) of single phase powellites before & after 600 keV Kr and 200 keV He irradiations.

Electron diffraction patterns corresponding to irradiated and unirradiated areas, shows that $CaMoO_4$ powellite phase in multiphase waste forms still keep good crystalline powellite phase under 600 keV Kr irradiation with a fluence of 2.5×10^{15} ions/cm^2 (corresponding to a dose of 5 dpa). Based on XRD observations in Fig. 9(b), single phase BaMoO4 exhibits similar radiation tolerance under either Kr or He irradiation at dose of 5 dpa, and there is no observed radiation-induced amorphization in these irradiated samples. Experiment results tell us that powellite phase in multiphase waste form exhibits the similar radiation tolerance/amorphization resistance to single powellite phase under the same radiation condition.

3. Future work

LANL will focus on characterization on the reference crystalline ceramics to further develop the crystalline ceramic waste form to incorporate combined HLW raffinate stream and/or TRU stream from fuels fabrication processes. FY15 activities include: (1) characterization of multiphase hollandite, (2) characterization of melter test ceramic waste forms from SRNL and INL, which includes chemical and structural information of crystalline phases and phase interfaces. High-spatial resolution characterization with transmission electron microscopy (TEM), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) elemental mapping, X-ray diffraction, micro-X ray diffraction and other characterization techniques will be performed to analyze crystallite structure, composition, structural and chemical homogeneity.

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